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Construction of Large Reaction Mechanisms

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October 9, 1981

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An algorithm has been developed to systematically and objectively generate tractable reaction mechanisms using as input information the species present, and their enthalpies, entropies, number of atoms, and number of bonds. The algorithm generates all possible reactions subject to the constraints of mass balance, energy, entropy, and number of bonds broken and formed. Bimolecular, unimolecular decomposition, addition and isomerization reactions are considered. Even the most expert kineticist can err (by omission) with mechanisms involving 50 or more species. This method reduces that error and still allows for the application of chemical intuition by the researcher.

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CONTENTS

CONSTRUCTION OF LARGE REACTION MECHANISMS

INTRODUCTION

Researchers are currently studying combustion reactions in an effort to gain new insights into fuel combustion efficiency and fuel safety. The understanding of combustion systems is often greatly aided through the use of computational models. However, the complexity of multispecies systems makes the modeling task formidable. The methodology presented here demonstrates the logical formulation of a reaction mechanism for a multispecies combustion system.

For the combustion modeler and the chemical modeler in general, the formulation of a complex mechanism consists of two major steps:

1. Specification of the molecules and molecular fragments to be included in the system.

2. Selection of the chemical reactions to be considered and included in the proposed mechanism.

Subsequent steps to complete the overall modeling process include:

3. Assignment of the rate constants to the selected reactions.

4. Solution of the time dependent coupled differential equations of the model's full mechanism.

5. Comparison of the output from the model with experimental data.

6. Performance of sensitivity analysis on the parametric input to the model.

The six steps are usually performed in the order listed, but not necessarily. This report is concerned mostly with Step 2, the selection of the chemical reactions in the mechanism. We will assume that the species involved have been previously specified (Step 1) and we will use a sample species set for illustrative purposes.

Frequently chemical kinetic mechanisms are the product of a researcher's expertise and feelings. However, it can be very difficult for the modeler to consider each of the possible reactions when constructing a reaction set from a given set of reactive species. Even a small species set can give rise to an extremely large reaction scheme. Typically combustion systems can have more than 30 species. If the modeler does not or cannot consider all possible reactions involving the given species, then it is possible that potentially important reactions will not be considered.

Usually there is some agreement among modelers as to the rate constants to assign to various reactions (Step 3). Many models are attacked because of rate constants that are possibly incorrect by one or two orders of magnitude (typical units of cm^3 $molecule^{-1}$ s^{-1}). However, one quickly realizes that omitting a potentially important reaction underestimates that rate constant by 13 or 14 orders of magnitude. (Omission sets a rate constant of zero versus a typical bimolecular rate constant value of 10^{13} to 10^{14} cm^3 $molecule^{-1}$ s^{-1}.) It is for this reason that it is quite important to *consider* (not necessarily include, but consider) all possible reactions. Even the most expert kineticist can easily err when it comes to mechanisms of 50 or more species. It should be mentioned parenthetically here that the difficulty in the eventual solution of the coupled differential equations (Step 4) is in the number of species, not the number of reactions, because the number of coupled differential equations is dictated by the number of species. A model of 900 reactions of 55 species is tractable.

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If a systematic procedure, or algorithm, which allows for the consideration of all possible reactions can be followed when constructing a reaction set, some of the uncertainty associated with the proposed mechanism can be eliminated. The organization of the mechanism is also enhanced, and the time required to construct the complete reaction set is decreased. Therefore, in an effort to reduce the arbitrariness inherent in Step 2, we present in this report a convenient algorithm by which modelers can quickly and automatically construct a complete reaction set. We assume for this analysis that all the relevant species which play a significant role in the mechanism have been specified.

SAMPLE SYSTEM AND NOTATION

In order to understand the use of the proposed algorithm, it will be discussed here in the context of an example system. Specifically, we formulated and used our algorithm as part of our effort model understanding the low-temperature n-butane oxidation phenomenon. Some of the criteria explained in the following section are specific to the n-butane oxidation system; however, most considerations are generally valid.

The set of reactive species used as a sample in this report is listed in Table 1. The column titled "Species" gives each species an eight character name (four computer words on our 16-bit machine). The name is for the convenience of the users; no exclusion criterion is based on the *name* of the species. Columns 2 through 4, NC, NH, and NO designate the number of carbons, hydrogens, and oxygens in the original molecule. Remember that the system of interest here is a C, H, O system. The algorithm can be easily modified to include other atomic species. Column 5 entitled NZ gives a number to each species. This number is mostly for internal accounting in the program. It is shown in the next section how selective numbering can aid in generating an additional criterion. Columns 6 and 7 are the $\Delta H_f(298)$ in kcal/mole and S(298) cal/(deg·mole), respectively, of the input molecules. These numbers can be found in the literature [1] or estimated using conventional means [2].

It will be helpful to understand the following discussion of the algorithm and the program itself, to introduce some notation. The set of stable molecules and molecular fragments (radicals) shall be called R. There are N species in R including a special species M which is explained later in this report. Let R(I), R(J), R(K), and R(L) represent the I, J, K, and L species within the set of the N chosen species. Indices I, J, K and L range independently over the entire set of N species. There is nothing to prohibit these indices from being equal. Throughout the text, and the program, I and J will index reactants and K and L will index products. Thus, all possibilities of two reactants forming two products are:

$$R(I) + R(J) \rightarrow R(K) + R(L). \tag{1}$$

We can represent Eq. (1) using matrix notation. The reactants portion of Eq. (1) are represented by the $N \times N$ matrix whose entries consist of all possible combinations of R(I) and R(J). Since there are N possible R(I) and independently N possible R(J), there are N^2 possible species combinations of R(I) + R(J).

As a simple example, consider the species set consisting of only A, B and C. We can represent all possible combinations of reactants involving these species by the entries in the following symmetric matrix:

$$\begin{bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{bmatrix}.$$

Similarly, this matrix also represents all possible combinations of products of bimolecular reactions involving these species. The special species M is included in the reaction set so that addition and unimolecular decomposition reactions are also available.

Thus, all possible reactions in the form of Eq. (1) can be represented as a mapping from one entry of the reactant matrix onto any one entry of the product matrix. For the species set A, B, C, the following are equivalent for the set R:

$$\begin{Bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{Bmatrix} \longrightarrow \begin{Bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{Bmatrix}.$$

There are N^2 entries in each matrix and thus $N^2 \times N^2 = N^4$ total reaction possibilities. Even for a relatively small set of species, the total number of possible reactions is formidable. There is an obvious need, therefore, to formulate criteria to eliminate many of the possible reactions quickly and automatically.

CRITERIA IN MECHANISM GENERATION

Appendix A lists program RXNGN, a FORTRAN program for generation of a reaction mechanism. The many criteria appearing in the program RXNGN will be discussed in this section but not necessarily in the order that they appear in the program. Generally, the criteria in the program appear in order of decreasing exclusion. The sooner a reaction fails a criterion and can be removed, the less criteria must be applied to that reaction. The development of criteria in the text will be ordered more along the lines of a chemical deductive process.

One of the most important criteria for the reactions to satisfy is mass balance. The input information on the number of carbons, hydrogens, and oxygens (columns 2, 3, and 4 of Table 1) is used for the mass balance computation (lines 83 to 89 of the program). As a programming note, we parenthetically point out that carbon balance is checked first, then hydrogen balance, and then oxygen balance. If the carbon balance fails, there is no need to check the hydrogen or oxygen balance (see program).

The number of possible reactions that may be eliminated by the mass balance criterion is entirely dependent on the specific species list, and, therefore, cannot be denoted generally in terms of the number of original species, N. The following discussion indicates the number of reactions that are eliminated by the imposition of each criterion, but the number indicated does *not* exclude those already eliminated by the mass balance criterion. Note that the number of reactions that may be eliminated on the basis of any one criterion is highly dependent on the order in which the criteria are imposed.

The next criterion to consider is that of simple permutation. Since it does not matter, for example, if A reacts with B, or B with A, all of the following denote the same reaction chemically:

$$A + B \rightarrow C + D$$

$$A + B \rightarrow D + C$$

$$B + A \rightarrow C + D$$

$$B + A \rightarrow D + C.$$

This repetition needs to be eliminated systematically. To illustrate the systematic elimination, we use the simple matrix. Label the upper and lower triangular region of each symmetric matrix x_1, x_2, x_3, x_4 such that:

$$\begin{Bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{Bmatrix} \longrightarrow \begin{Bmatrix} AA & AB & AC \\ BA & BB & BC \\ CA & CB & CC \end{Bmatrix}$$

becomes

$$\begin{bmatrix} AA & & x_2 \\ & BB & \\ x_1 & & CC \end{bmatrix} \longrightarrow \begin{bmatrix} AA & & x_4 \\ & BB & \\ x_3 & & CC \end{bmatrix}.$$

Since the product and reactant matrices are symmetric about the main diagonal, x_1 and x_2 of the reactant matrix and x_3 and x_4 of the product matrix contain equivalent entries. To eliminate the repetition, we eliminate all the entries of either x_1 or x_2 and x_3 or x_4. If we arbitrarily choose to eliminate x_2 and x_4, we now have:

$$\begin{bmatrix} AA & & \\ & BB & \\ x_1 & & CC \end{bmatrix} \longrightarrow \begin{bmatrix} AA & & \\ & BB & \\ x_3 & & CC \end{bmatrix}.$$

By eliminating the entries of x_2 and x_4, we eliminate $(N-1) + (N-2) + (N-3) + \ldots + 1 = \frac{N(N-1)}{2}$ entries from each matrix. The number of reaction possibilities we have eliminated by imposing this criterion is:

$$\begin{bmatrix}\text{The number of entries eliminated}\\ \text{from the reactant matrix.}\end{bmatrix} \times \begin{bmatrix}\text{Total number of entries}\\ \text{in the product matrix.}\end{bmatrix}$$

$$+ \begin{bmatrix}\text{The number of entries remaining}\\ \text{in the reactant matrix.}\end{bmatrix} \times \begin{bmatrix}\text{The number of entries eliminated}\\ \text{from the product matrix.}\end{bmatrix},$$

which in terms of N is:

$$\frac{N(N-1)}{2} \cdot N^2 + N^2 - \frac{N(N-1)}{2} \cdot \left[\frac{N(N-1)}{2}\right] = \frac{N^2(N-1)}{4}(3N+1)$$

reaction possibilities eliminated. The number of entries remaining in each matrix is $N^2 - N(N-1)/2 = N(N+1)/2$. Since there are $(N)(N+1)/2$ entries remaining in each matrix, and since with the remaining entries all mappings are possible, there are

$$\frac{N(N+1)}{2} \cdot \frac{N(N+1)}{2} = \left[\frac{N(N+1)}{2}\right]^2$$

possible reactions remaining to be considered.

Simple permutations are eliminated by the code on line 91 in the program in Appendix A.

Nonreactions or "identity" reactions (i.e., $A + B \rightarrow A + B$ or $A + A \rightarrow A + A$, etc.) must be eliminated. Thus, our criterion is that if $I = K$ and $J = L$, or $I = L$ and $J = L$, or $I = K$ and $J = K$, or $I = L$ and $J = K$, then the reaction is eliminated from consideration. These reaction types are *exact* mappings from an entry in the reactant matrix onto the same entry in the product matrix. Since there are the same number of these *identity* reactions as there are remaining entries in each matrix, by eliminating these *identity* reactions from consideration, we eliminate $N(N+1)/2$ possible reactions. The number of remaining possible reactions is then

$$\left[\frac{N(N+1)}{2}\right]^2 - \frac{N(N+1)}{2} = \frac{(N-1)(N)(N+1)(N+2)}{4}.$$

The next applicable criterion is *no reactions with certain species* or, if on the basis of experimental evidence it can be determined that certain species appear in *negligible* relative concentrations or are unreactive, then one may want to consider those species as products only, or eliminate them from consideration. If a certain species is to be considered as a product only, it is necessary to eliminate all possible reactions involving that species as a reactant going to all possible products. For any given species there are exactly N remaining entries in the matrix which contain that species. For example, if we are interested in species A, we find that for the case where $N=3$, there are exactly 3 entries which contain at least one A.

$$\begin{bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{bmatrix}$$

The number of possible product entries to which a given reactant entry can go is the number of entries on the product side minus one. We subtract one from the number of entries on the product side to avoid double counting those reactions which we eliminated previously by imposing the *identity reaction* criterion. For example, if we wish to eliminate all reactions involving species A as a reactant, then we do not want to count the following reactions as being eliminated by this criterion:

$$A + A \rightarrow A + A$$

$$B + A \rightarrow B + A$$

$$C + A \rightarrow C + A.$$

Thus, removing a given species from consideration as a reactant eliminates:

$$N \cdot \begin{array}{c}\text{Number of entries}\\ \text{on product side}\end{array} - 1$$

$$= N \cdot \frac{N(N+1)}{2} - 1$$

$$= N \cdot \frac{N^2 + N - 2}{2} \text{ possible reactions.}$$

If for some reason, after the species set has been chosen, we wish to to eliminate all possible reactions involving a given species as both products and reactants, then we eliminate the possible reactions involving:

$$\left\{\begin{array}{l}\text{A reactant pair having at}\\ \text{least one of the pairs as}\\ \text{species to be eliminated.}\end{array}\right\} \xrightarrow[\text{to}]{\text{going}} \left\{\begin{array}{l}\text{All products minus}\\ \textit{exact mappings}\\ \end{array}\right\}$$

$$\left\{\begin{array}{l}\text{The remaining}\\ \text{reactant pairs.}\end{array}\right\} \xrightarrow[\text{to}]{\text{going}} \left\{\begin{array}{l}\text{Product pairs which have}\\ \text{at least one of the pairs}\\ \text{being the species to be}\\ \text{eliminated}\end{array}\right\}.$$

Or in terms of N we eliminate:

$$N \cdot \frac{(N+1)N}{2} - 1 + \frac{N(N+1)}{2} - 1 \cdot N = (N^2 - 1) \cdot N \text{ possible reactions.}$$

(For an example of this criterion see lines 112 and 113 in Appendix A.)

Because radicals usually are more reactive than stable species, reactions involving two radicals, or one radical and one stable species as reactants, are much more likely to occur at low temperatures than

reactions involving two stable species. A fifth possible criterion is to eliminate all possible reactions involving two stable species as reactants. This criterion is applicable to our low temperature oxidation of n-butane, but is not applicable in many other cases. Letting NSP represent the number of stable species in the species set, we find that the number of stable reactant pairs in the reactants matrix is NSP (NSP+1)/2. We now wish to eliminate all reactant pairs consisting of two stable species which go to all possible products minus *exact mappings*. In our simple example, let us assume A is the only stable species.

$$\begin{Bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{Bmatrix} \longrightarrow \begin{Bmatrix} AA & & \\ BA & BB & \\ CA & CB & CC \end{Bmatrix}$$

We wish to eliminate the following possible reactions:

$$A + A \rightarrow B + A$$

$$A + A \rightarrow B + B$$

$$A + A \rightarrow C + A$$

$$A + A \rightarrow C + B$$

$$A + A \rightarrow C + C.$$

(Note: $A + A \rightarrow A + A$ was eliminated under the *exact mapping* criterion.) Here (with $N = 3$ and $NSP = 1$) we eliminate five possible reactions. In general with NSP stable species and N total species, we eliminate

$$\frac{NSP(NSP+1)}{2} \cdot \frac{N(N+1)}{2} - 1$$

"possible reactions."

This criterion is applied in the program in Appendix A by line 104. The species in the input file were carefully grouped (column NZ) so that all stable species were numbered after all the radicals, and the special species M. In Table 1 there are 29 stable species.

It is useful to limit the reactions also on an enthalpy and free energy basis. With the input enthalpy (ΔH_f(298), column 6 of Table 1) and entropy S(298), column 7 of Table 1) it is easy to calculate ΔH_R and ΔG_R (lines 131 to 133 of program RXNGN in Appendix A):

$$\Delta H_R = \Delta H_p - \Delta H_r$$

$$\Delta S_R = \Delta S_p - \Delta S_r$$

$$\Delta G_R = \Delta H_R - T\Delta S_R,$$

where T represents temperature, and the subscripts R, p, r represent reaction, products, and reactants.

One can then set limits for acceptable ΔG_R and ΔH_R. Ideally, of course, ΔG_R should be less than or equal to zero. However, since measurements of ΔH_f(298) and S(298) are not perfect, and since some estimated values for those quantities were used, it is advisable to set the cutoff for ΔG_R above the theoretical limiting value of 0.0.

In large complex chemical systems, such as combustion, endothermic reactions occur. In our example program we used a cutoff value for ΔH_R of 35 kcal/mole (line 134 of program RXNGN in Appendix A).

The next two criteria we used involve a knowledge of the structure of each molecule. In a carbon, hydrogen, oxygen system there are five major types of bonds: 1) carbon-hydrogen (the number of

carbon-hydrogen bonds is designated NCH); 2) carbon-carbon (NCC); 3) carbon-oxygen (NCO); 4) oxygen-oxygen (NOO); and 5) oxygen-hydrogen (NOH). Oxygen-oxygen bonds are important in low-temperature *n*-butane oxidation because of the prevalence of peroxides; this bond type might be unimportant in other systems. Logically, three atomic species should give rise to six bond types. The sixth type here is hydrogen-hydrogen, and since that occurs in only one molecule in our system hydrogen (H_2), NHH is not included. A double bond would count as two bonds. For example, NCC of ethene is 2. Table 2 lists the numbers of each of these five-bond types for our input data set. The first column (NZ) corresponds to the NZ column of Table 1. (Note that Table 2 concatenated to Table 1 is essentially the input file to program RXNGN.)

Using the number of each type of bond as input data, there are two apparent restrictions to impose. First, limit the total bond change between products and reactants; and second, put limits on the change in each type of bond between products and reactants.

It must be kept in mind that the purpose is to generate a set of elementary (one-step) reactions. If the products have, for example, four carbon-carbon bonds and the reactants have nine, it is difficult to see how one elementary chemical step can break five carbon-carbon bonds. The number of each type of bond broken is subtracted from the number of each type of bond formed (lines 138 to 142 of program RXNGN in Appendix A). Specific limits are then imposed for the change in total number of bonds (lines 148 and 152 to 154) and the change in number of each type of bond (lines 157 to 161) (Appendix A).

A special species M, without any mass, (i.e., the number of carbons, hydrogens, and oxygens in it are all zero) is used to allow for unimolecular decompositions, addition reactions, and single counting of isomerization reactions.

Unimolecular decomposition: $A + M \rightarrow B + C$.

Addition Reaction: $A + B \rightarrow C + M$.

Isomerization: (if A and B are isomers then all of the following satisfy mass balance):

$$A + M \rightarrow B + M$$

$$A + B \rightarrow B + B$$

$$A + C \rightarrow B + C\text{ , etc.}$$

We eliminate all isomerizations except for the first reaction listed. So that the program is more general, M does not have to be a specific species number (NZ), thus when numbering the species, no special number is reserved for M. The program finds what the species number of M is (lines 117 to 122). The species number of M is not used for the unimolecular decompositions or additions. The redundancy of isomerizations is eliminated by the code on lines 124 and 125 of Appendix A.

CRITERIA APPLIED TO n-BUTANE OXIDATION

We now want to examine the results of applying our general criteria developed in the first section of this report to the species set which we considered in modeling the low-temperature oxidation of n-butane. Our species set consisted of 56 species (27 radicals, 28 stable species, and the special species M, see Table 1). As we noted earlier for the reaction $R(I) + R(J) \rightarrow R(K) + R(L)$ with the only restriction being that I, J, K, and L be members of our species list consisting of N species, there originally existed N^4 or in this case $(56)^4 = 9{,}8348{,}496$ possible reactions to be considered.

With 56 species both the reactants matrix and the products matrix were originally 56×56 square symmetric matrices composed of 3136 entries each. By imposing the permutation criterion, (which

essentially eliminates all entries above or below the main diagonal from each matrix) we eliminated $N(N-1)/2 = 56(55)/2 = 1540$ entries from both the products and reactants matrix. The number of reaction possibilities which we eliminated was:

$$N^2 \frac{(N-1)}{4}[3N+1] = (56)^2 \cdot \frac{55}{4}[3(56)+1] = 7{,}287{,}280.$$

The number of reaction possibilities which remained was $(N(N+1))^2 = 2{,}547{,}216$.

By imposing the *identity* reaction criterion, we eliminated $N(N+1)/2$ possible reactions or, in this case, $56(57)/2 = 1596$ reactions. Thus by imposing the first two criteria, we eliminated 7,290,416 possible reactions.

For our particular system we selected three stable species to act as products only. As shown earlier, removing a given species from consideration as a reactant results in the elimination of $N(N^2 + N - 2)/2$ possible reactions or in this case:

$$\text{(three species) } (56)56^2 + 56 - 2)/2 = 267{,}960$$

possible reactions were eliminated.

We imposed the criterion to eliminate all possible reactions involving two stable species as reactants. Since in our particular species set there were 28 stable species, by applying this criterion we eliminated: $\frac{NSP(NSP+1)}{2} \cdot \frac{N(N+1)}{2} - 1 = \frac{28(29)}{2} \cdot \frac{56(57)}{2} - 1 = 647{,}975$ possible reactions. Before taking the mass balance criterion into consideration and as a result of imposing these four criteria, our reaction set consisted of 1,628,145 possible reactions. In our example the mass balance criterion was, next to the permutation criterion, the most restrictive. Every species in our system was composed of some number and combination of H atoms, C atoms, and O atoms. The mass balance criterion was then, if one of the following was not true, the reaction was eliminated:

$$C(K) + C(L) - C(J) - C(I) = 0$$

$$H(K) + H(L) - H(J) - H(I) = 0$$

$$O(K) + O(L) - O(J) - O(I) = 0.$$

Using only three criteria, mass balance and elimination of permutation and redundancy reduced the set from $(56)^4 = 9{,}834{,}496$ to a much more manageable 13,092.

Imposition of the thermodynamic criteria (limiting value for ΔH_R and ΔG_R) reduced the reaction set by 3282 reactions. The bond breaking and forming criteria reduced the set by 2687 reactions. By allowing isomerizations to occur only with the special species M, the mechanism shortened by another 1080 reactions. The specific case criterion of no bimolecular reactions of stable species eliminated 539 reactions. The additional specific checks (see listing of program in Appendix A) eliminated 2255 reactions and brought the set down 3249 reactions. Remember, the amount each criterion reduces the total is dependent on the order in which the criteria are applied.

Thirty-two hundred reactions are still quite a lot, but few enough so that visual inspection is a realistic task. We examined the mechanism with the aid of the search programs which are described in the next section. Many of the remaining reactions were not one-step reactions. In fact, many reactions appeared to be two-step reactions and both of the individual steps were already in the mechanism. Below are three such examples where part (a) is an obvious two-step mechanism and parts (b) and (c) are the two individual reaction steps which were already part of the mechanism.

1) a. $CH_3CO + O_2 \rightarrow CH_3O_2 + CO$

b. $CH_3CO + M \rightarrow CH_3 + CO$

c. $O_2 + CH_3 \rightarrow CH_3O_2 + M$

2) a. $CH_3CO + n\text{-}C_3H_7 \rightarrow C_4H_{10} + CO$

b. $CH_3CO + M \rightarrow CH_3 + CO$

c. $CH_3 + n\text{-}C_3H_7 \rightarrow C_4H_{10} + M$

3) a. $CH_3OO + i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_7O_2 + CH_3$

b. $CH_3OO + M \rightarrow CH_3 + O_2$

c. $O_2 + i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_7O_2 + M$

The output of program RXNGN is not reproduced here because it is excessively long; however, the outputs of the two search programs described in the next section are formatted the same. (See Tables 3 and 4.) For each reaction, the reactants and products with their respective species numbers; the ΔH_R; the ΔG_R; the number of reactions tried; the number of reactions found; the net change of CH, CC, CO, OO, and OH bonds; and the total net bond change, are tabulated. The species numbers are for convenience and give the subsequent search programs something to key on. The number tried is the number of reactions that pass the mass balance, redundancy and permutation criteria. The number found represents those reactions that have passed all the imposed criteria. The bond change numbers represent the sum of that type of bond in the products minus the sum of that type of bond in the reactants. (Note that these numbers can be negative.) The column entitled NET is the sum of the absolute values of each of the preceding five columns.

From the original $(56)^4 = 9,834,496$ possible reactions, we were able to construct a reasonable reaction set by formulating a logically ordered set of general and specific rational criteria, and imposing these criteria upon all of the possible reactions. We are thus able, to a great extent, to remove the process of reaction set formulation out of the intuitive domain. Imposing the formulated rational criteria allowed us to systematically arrive at a reaction set consisting of about 850 reactions, after originally considering over nine million possible reactions.

SEARCH CAPABILITIES

Three programs were developed to assist in the examination of the mechanism. These three programs look at the file created by the program RXNGN (Appendix A).

The capability to search through the data file is very powerful. For example, program SELET (reproduced in Appendix B) searches the reaction file for all reactions in which a particular input species is found as a reactant, or as a product; or as either a reactant or a product. In this way, one can quickly see the formation and destruction pathways a particular species takes through the overall mechanism. If the user is, for example, interested specifically in methanol, the reaction set may be searched for the reaction in which methanol appears. Alternatively, one could search for those reactions that create hydroxy radicals. It is, of course, possible that from examination of this *edited* output from the search program, the chemist might feel that a reaction that is felt to be important intuitively is missing. This means that either (1) a key species has been omitted from the original data file input to RXNGN; or (2) one of the criteria used in RXNGN is too stringent and excludes important reactions. Chemical knowledge and intuition are still important in the use of these algorithms.

Table 3 shows some sample output of program SELET. All the reactions in which methanol (species number 28) occurred as a reactant, were found.

Program SLRXT (reproduced in Appendix C) permits the user to search for reactions of classes of reactants. For example, one could examine all the reactions that occur with alkyl radicals by inputting the species numbers of all the alkyl radicals. The program also allows complementary reactants, that is, one could examine all the reactions that occur between alkyl radicals and alcohols by specifying all the alkyl radicals and then specifying all the species numbers of all the alcohols as complementary reactants. Table 4 shows this situation as a sample output of SLXRT.

The last utility program is entitled RLIST (reproduced in Appendix D). This simple program allows the listing of the reaction file in a shortened version so that there is room (in the right hand *margin*) to annotate the file. The other two programs (SELET and SLRXT) reproduce the input file exactly as it is, merely selecting out certain reactions. Program RLIST is merely a convenience and is included as Appendix D for completeness.

CONCLUSION

We have formulated an algorithm to systematically produce tractable reaction mechanisms for computational modeling of complex chemical kinetic systems. The additional searching algorithms provide a very powerful observational and educational tool as they permit the user to study thoroughly the entire reaction mechanism.

REFERENCES

1. D.R. Stull and H. Prophet, editors, *JANAF Thermochemical Tables*, 2nd ed., NSRDS, NBS-37, U.S. Govt. Printing Office (1971).

2. Sidney W. Benson, *Thermochemical Kinetics*, 2nd edition, J. Wiley and Sons, N.Y., 1976.

LIST OF SYMBOLS

Symbol	Description	Units
A, B, C, D	Designation for arbitrary species	
I, J	Indices of reactant species	
K, L	Indices of product species	
M	Special species	
N	Number of species in set R	
NC	Number of carbon atoms	
NCC	Number of carbon-carbon bonds	
NCH	Number of carbon-hydrogen bonds	
NCO	Number of carbon-oxygen bonds	
NH	Number of hydrogen atoms	
NHH	Number of hydrogen-hydrogen bonds	
NO	Number of oxygen atoms	
NOO	Number of oxygen-oxygen bonds	
NOH	Number of oxygen-hydrogen bonds	
NSP	Number of stable species	
NZ	Species number of a specific species	
R	The set of all input species	
R(index)	The indexed species	
S(298)	Entropy at 298K	cal/(deg·mole)
T	Temperature	degrees K
$X_1X_2X_3X_4$	Areas of particular matrix under discussion	
ΔG_R	Free energy change of reaction	kcal/mole
$\Delta H_f(298)$	Heat of formation at 298K	kcal/mole
ΔH_R	Enthalpy change of reaction	kcal/mole
Subscript p	Products	
Subscript r	Reactants	
Subscript R	Reaction	

Table 1 — Species and Parameters

SPECIES	NC	NH	NO	NZ	DELTA H	S
O*	0	0	1	24	59.5	38.5
O2	0	0	2	48	0.0	49.0
H*	0	1	0	1	52.1	27.4
OH*	0	1	1	2	9.4	43.9
HO2*	0	1	2	3	5.0	54.4
H2O	0	2	1	49	-57.8	45.1
CH4	1	4	0	50	-17.9	44.5
CO	1	0	1	44	-26.4	47.3
CO2	1	0	2	40	-94.0	51.2
CH3O*	1	3	1	5	3.5	55.2
CH3OH	1	4	1	28	-48.1	57.3
CH3O2*	1	3	2	6	6.7	65.3
C2H4	2	4	0	29	12.5	52.4
C2H5*	2	5	0	7	26.5	58.0
C2H6	2	6	0	30	-20.2	54.9
CH3CO*	2	3	1	8	-5.4	64.5
CH3CHO	2	4	1	31	-39.7	63.2
CH3CH2O*	2	5	1	9	-4.0	65.3
C2H5OO*	2	5	2	10	-5.0	76.4
C3H6	3	6	0	32	4.9	63.8
C3H7*-N	3	7	0	11	21.0	68.5
C3H7*-I	3	7	0	12	17.6	66.7
C2H3CHO	3	4	1	33	-17.7	69.1
CH3COCH3	3	6	1	34	-51.7	70.5
C3H7O-I*	3	7	1	13	-12.6	71.8
C4H8TBTE	4	8	0	35	-2.7	70.9
C4H81BTE	4	8	0	36	0.0	73.6
C4H9-N*	4	9	0	14	16.8	76.6
C4H9-S*	4	9	0	15	13.7	75.2
C4H10NBT	4	10	0	37	-30.2	74.1
C4H8OTHF	4	8	1	38	-44.0	73.6
C4H9OH	4	10	1	39	-65.6	86.8
C4H9O*	4	9	1	16	-14.0	76.5
C4H9O2*S	4	9	2	27	-17.8	93.5
M	0	0	0	4	0.0	0.0
H2O2	0	2	2	41	-32.6	56.0
HCHO	1	2	1	42	-26.0	52.3
HCO*	1	1	1	17	9.0	53.7
CH3OOH	1	4	2	43	-31.3	67.5
CH3*	1	3	0	26	34.3	46.4
MECHO*ET	4	9	1	18	-17.5	89.6
CH3COOOH	2	4	3	45	-80.9	80.4
CH3COO*	2	3	2	19	-49.6	66.6
MCHOOHET	4	10	2	46	-53.3	92.1
C4H9OOH	4	10	2	47	-49.0	94.1
C4H9OO*	4	9	2	20	-13.5	96.0
CH3COOO*	2	3	3	21	-29.0	78.9
C2H5OOH	2	6	2	51	-40.5	76.3
C3H7O*	3	7	1	25	-9.9	75.3
C3H7OO*	3	7	2	22	-8.5	88.2
MCHOO*M	3	7	2	23	-12.9	84.1
C3H7OOH	3	8	2	52	-44.0	84.6
MCHOOHM	3	8	2	53	-48.4	82.7
C3H8	3	8	0	54	-24.8	64.5
C4H823EB	4	8	1	56	-23.9	84.6
H2	0	2	0	55	0.0	31.2

Table 2 — Numbers of Bond Types

NZ	NCH	NCC	NCO	NOO	NOH
1	0	0	0	0	0
2	0	0	0	0	1
3	0	0	0	1	1
4	0	0	0	0	0
5	3	0	1	0	0
6	3	0	1	1	0
7	5	1	0	0	0
8	3	1	2	0	0
9	5	1	1	0	0
10	5	1	1	1	0
11	7	2	0	0	0
12	7	2	0	0	0
13	7	2	1	0	0
14	9	3	0	0	0
15	9	3	0	0	0
16	9	3	1	0	0
17	1	0	2	0	0
18	9	3	1	0	0
19	3	1	3	0	0
20	9	3	1	1	0
21	3	1	3	1	0
22	7	2	1	1	0
23	7	2	1	1	0
24	0	0	0	0	0
25	7	2	1	0	0
26	3	0	0	0	0
27	9	3	1	1	0
28	3	0	1	0	1
29	4	2	0	0	0
30	6	1	0	0	0
31	4	1	2	0	0
32	6	3	0	0	0
33	4	3	2	0	0
34	6	2	2	0	0
35	8	4	0	0	0
36	8	4	0	0	0
37	10	3	0	0	0
38	8	3	2	0	0
39	9	3	1	0	1
40	0	0	4	0	0
41	0	0	0	1	2
42	2	0	2	0	0
43	3	0	1	1	1
44	0	0	2	0	0
45	3	1	3	1	1
46	9	3	1	1	1
47	9	3	1	1	1
48	0	0	0	1	0
49	0	0	0	0	2
50	4	0	0	0	0
51	5	1	1	1	1
52	7	2	1	1	1
53	7	2	1	1	1
54	8	2	0	0	0
55	0	0	0	0	0
56	8	3	2	0	0

Table 3

REACTIONS INVOLVING SPECIES NUMBER 28 AS A REACTANT

REACTANTS		PRODUCTS	DELH	DELG	#TRD	#FND	NCHD	NCCD	NCOD	NOOD	NOHD	NET
O* (24) + CH3OH (28)	->	OH* (2) + CH3O* (5)	1.5	.5	22	8	0	0	0	0	0	0
H* (1) + CH3OH (28)	->	CH3O* (5) + H2 (55)	-.5	-1.0	789	132	0	0	0	0	-1	1
OH* (2) + CH3OH (28)	->	H2O (49) + CH3O* (5)	-15.6	-15.3	1198	214	0	0	0	0	0	0
HO2* (3) + CH3OH (28)	->	CH3O* (5) + H2O2 (41)	14.0	14.1	1662	278	0	0	0	0	0	0
CH3OH (28) + CH3O2* (6)	->	CH3O* (5) + CH3OOH (43)	13.6	13.6	3737	529	0	0	0	0	0	0
CH3OH (28) + C2H5* (7)	->	CH3O* (5) + C2H6 (30)	4.9	6.4	3754	531	1	0	0	0	-1	2
CH3OH (28) + CH3CO* (8)	->	OH* (2) + CH3COCH3(34)	11.2	13.4	3762	532	0	1	-1	0	0	2
CH3OH (28) + CH3CO* (8)	->	CH3O* (5) + CH3CHO (31)	17.3	18.3	3765	533	1	0	0	0	-1	2
CH3OH (28) + C2H5OO* (10)	->	CH3O* (5) + C2H5OOH (51)	16.1	16.8	3802	534	0	0	0	0	0	0
CH3OH (28) + C2H5OO* (10)	->	CH3CH2O*(9) + CH3OOH (43)	17.8	18.1	3803	535	0	0	0	0	0	0
CH3OH (28) + C3H7*-N (11)	->	CH3O* (5) + C3H8 (54)	5.8	7.6	3830	538	1	0	0	0	-1	2
CH3OH (28) + C4H9-N* (14)	->	CH3O* (5) + C4H10NBT(37)	4.6	6.0	3931	544	1	0	0	0	-1	2
CH3OH (28) + C4H9-S* (15)	->	CH3O* (5) + C4H10NBT(37)	7.7	8.7	3939	549	1	0	0	0	-1	2
CH3OH (28) + C4H9O* (16)	->	CH3O* (5) + C4H9OH (39)	-.0	-2.4	3973	554	0	0	0	0	0	0
CH3OH (28) + HCO* (17)	->	OH* (2) + CH3CHO (31)	8.8	10.0	4013	562	0	1	-1	0	0	2
CH3OH (28) + HCO* (17)	->	CH3O* (5) + HCHO (42)	16.6	17.6	4016	563	1	0	0	0	-1	2
CH3OH (28) + CH3* (26)	->	CH4 (50) + CH3O* (5)	-.6	.6	4022	565	1	0	0	0	-1	2
CH3OH (28) + C4H9OO* (20)	->	CH3O* (5) + C4H9OOH (47)	16.1	17.3	4061	567	0	0	0	0	0	0
CH3OH (28) + CH3COOO*(21)	->	CH3O* (5) + CH3COOOH(45)	-.3	-.1	4072	574	0	0	0	0	0	0
CH3OH (28) + C3H7OO* (22)	->	CH3O* (5) + C3H7OOH (52)	16.1	17.8	4101	576	0	0	0	0	0	0
CH3OH (28) + C3H7OO* (22)	->	CH3OOH (43) + C3H7O* (25)	15.4	16.2	4108	578	0	0	0	0	0	0
CH3OH (28) + HCHOO+M (23)	->	CH3O* (5) + HCHOOHM (53)	16.1	17.1	4115	579	0	0	0	0	0	0
CH3OH (28) + HCHOO+M (23)	->	C3H7O-I*(13) + CH3OOH (43)	17.1	17.7	4118	581	0	0	0	0	0	0

SELECTION PROCESS FINISHED. A TOTAL OF 21 SELECTED.

Table 4

REACTIONS INVOLVING SPECIES AS REACTANTS-> 7 11 12 14 15 26
COMPLEMENTARY REACTANTS -> 28 39

REACTANTS		PRODUCTS	DELH	DELG	#TRD	#FND	NCHD	NCCD	NCOD	NOOD	NOHD	NET
CH3OH (28) + C2H5* (7)	->	CH3O* (5) + C2H6 (30)	4.9	6.4	3754	531	1	0	0	0	-1	2
CH3OH (28) + C3H7*-N (11)	->	CH3O* (5) + C3H8 (54)	5.8	7.6	3830	538	1	0	0	0	-1	2
CH3OH (28) + C4H9-N* (14)	->	CH3O* (5) + C4H10NBT(37)	4.6	6.0	3931	544	1	0	0	0	-1	2
CH3OH (28) + C4H9-S* (15)	->	CH3O* (5) + C4H10NBT(37)	7.7	8.7	3939	549	1	0	0	0	-1	2
CH3OH (28) + CH3* (26)	->	CH4 (50) + CH3O* (5)	-.6	.6	4022	565	1	0	0	0	-1	2
C2H5* (7) + C4H9OH (39)	->	C2H6 (30) + C4H9O* (16)	4.9	8.9	5179	945	1	0	0	0	-1	2
C3H7*-N (11) + C4H9OH (39)	->	C4H98* (16) + C3H8 (54)	5.8	10.1	7800	1893	1	0	0	0	-1	2
C3H7*-I (12) + C4H9OH (39)	->	C4H98* (16) + C3H8 (54)	9.2	12.9	8175	2053	1	0	0	0	-1	2
C4H9-N* (14) + C4H9OH (39)	->	C4H10NBT(37) + C4H9O* (16)	4.6	8.4	9809	2385	1	0	0	0	-1	2
C4H9OH (39) + CH3* (26)	->	CH4 (50) + C4H9O* (16)	-.6	3.0	10792	2600	1	0	0	0	-1	2

SELECTION PROCESS FINISHED. A TOTAL OF 10 SELECTED.

Appendix A
PROGRAM RXNGN

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FTN4,L
      PROGRAM RXNGN(3,99), REV. 800709 DOREN INDRITZ
C     VERSION 800709 FOR HEWLETT PACKARD MINICOMPUTER
C      IDEA BUILT UPON WALT SHAUB'S REACTION GENERATOR.
C
C     PROGRAM GENERATES ALL POSSIBLE REACTIONS, GIVEN INPUT SPECIES
C      (UP TO 100), SUBJECT TO VARIOUS CONSTRAINTS LISTED
C      THROUGHOUT THE COMMENTS IN THE PROGRAM.
C
C      CURRENTLY DIMENSIONED FOR UP TO 100 INPUT SPECIES.
      DIMENSION NAME(4,100),ENTL(100),NZ(100),ENTR(100)
      DIMENSION NCH(100),NCC(100),NCO(100),NOO(100),NOH(100)
      INTEGER C(100),H(100),O(100),IP(5)
      DATA II,JJ,TEMP/0,0,298.0/
C
C    FORMATS
C
  100 FORMAT(' ENTER LU OF DATA CASSETTE: ')
  101 FORMAT(1X,6I9)
  102 FORMAT(' IER = ',I8)
  103 FORMAT(I2)
  104 FORMAT(1X,4A2,4X,I1,3X,I2,4X,I1,4X,I2,2X,F10.3,2X,F10.3)
  105 FORMAT(2X,4A2,4X,I1,3X,I2,4X,I1,4X,I2,2X,F10.1,2X,F10.1)
  106 FORMAT('1 REACTION GENERATOR N-BUTANE COOL FLAME'///)
  107 FORMAT(2X,4A2,'(',I2,')',3H + ,4A2,'(',I2,')',4H -> ,
     +       4A2,'(',I2,')',3H + ,4A2,'(',I2,')',2X,F10.1,2X,
     +       F10.1,1X,I5,I6,6I5)
  108 FORMAT('1',9X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
     &       3X,'#TRD',2X,'#FND',2X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
     &       'NOOD',1X,'NOHD',2X,'NET')
  109 FORMAT(' LEN = ',I10)
  110 FORMAT(////' TOTAL REACTIONS EXAMINED = ',I10)
  111 FORMAT(6I3)
  112 FORMAT(1H1,7X,'NZ',6X,'NCH',6X,'NCC',6X,'NCO',6X,'NOO',6X,'NOH')
  113 FORMAT(' ENTER LU OF OUTPUT DEVICE')
  114 FORMAT(' RXNGN HAS FINISHED ',I8,' REACTIONS EXAMINED.' 'NUMBER FOUND
     &       = ',I6)
C
C     GET LOGICAL UNIT NUMBER (LU) OF DIALOGUE DEVICE.
      CALL RMPAR(IP)
C
C     OBTAIN LU OF INPUT DEVICE (CURRENTLY THE PROGRAM IS SET UP
C      TO READ THE INPUT FILE OFF A CASSETTE.  THAT CAN BE CHANGED
C      WITHOUT TOO MUCH DIFFICULTY.)
      WRITE(IP(1),100)
      READ(IP(1),*) IN
C     OBTAIN LU OF LIST DEVICE
      WRITE(IP(1),113)
      READ(IP(1),*) LP
C     NOTE THAT OUTPUT DEVICE CAN BE TO A MAG TAPE (LU = 8 OR 18
C      ON THIS SYSTEM).  IF SO, A CONTROL WORD INTERNAL TO THE
C      PROGRAM, IS NEEDED.
      ICNTL = 100B + LP
C     WRITE OUT TITLE
      WRITE(LP,106)
```

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C      READ IN DATA FROM CASSETTE
C      SEE SAMPLE DATA FILE FOR FORMAT.
       READ(IN,*) N
       DO 15 I=1,N
       READ(IN,104) (NAME(I2,I),I2=1,4),C(I),H(I),O(I),NZ(I),ENTL(I),
      +              ENTR(I)
       WRITE(LP,105)(NAME(I2,I),I2=1,4),C(I),H(I),O(I),NZ(I),ENTL(I),
      +              ENTR(I)
       ENTR(I) = ENTR(I)/1000.0
   15  CONTINUE
C      READ IN NUMBER OF THE DIFFERENT TYPES OF BONDS FROM DATA FILE.
C
       WRITE(LP,112)
       DO 200 I = 1, N
       READ(IN,111) NC,NCH(NC),NCC(NC),NCO(NC),NOO(NC),NOH(NC)
  200  CONTINUE
       WRITE(LP,101) (I,NCH(I),NCC(I),NCO(I),NOO(I),NOH(I),I=1,N)
C
C
       WRITE(LP,108)
C
C      LOOP THROUGH ALL POSSIBLE COMBINATIONS OF THE INPUT SPECIES.
C
       DO 50 I=1,N
       DO 40 J=1,N
       DO 30 K=1,N
       DO 20 L=1,N
C      CHECK FOR MASS BALANCE
       T1=(C(K)+C(L))-(C(J)+C(I))
       IF(ABS(T1).GT.0.01) GO TO 20
       T2=(H(K)+H(L))-(H(J)+H(I))
       IF(ABS(T2).GT.0.01) GO TO 20
       T3=(O(K)+O(L))-(O(J)+O(I))
       IF(ABS(T3).GT.0.01) GO TO 20
C      CHECK IF REACTION HAS BEEN DONE BEFORE
       IF(K.GT.L.OR. I.GT.J) GO TO 20
C      CHECK FOR SIMPLE PERMUTATIONS OF REACTANT/PRODUCT PAIRS
       IF(I.EQ.K.AND.J.EQ.L ) GO TO 20
       IF(I.EQ.L.AND.J.EQ.L ) GO TO 20
       IF(I.EQ.K.AND.J.EQ.K ) GO TO 20
       IF(I.EQ.L.AND.J.EQ.K ) GO TO 20
       II=II+1
C      DON'T ALLOW REACTIONS OF STABLE SPECIES.
C      THIS IS AN EXAMPLE OF A REASONABLE CRITERION THAT THE USER
C       MIGHT IMPOSE BASED ON PRIOR KNOWLEDGE OF THE SYSTEM.
C       NOTE: HERE THE DATA FILE HAS BEEN SET UP IN A SPECIAL WAY
C         TO GROUP ALL STABLE SPECIES SEPARATELY FROM ALL RADICALS
C          I.E., THE RADICALS HAVE SPECIE NUMBERS > 27.
       IF(NZ(I) .GT. 27 .AND. NZ(J) .GT. 27) GOTO 20
C
       IA = NZ(I)
       JA = NZ(J)
       KA = NZ(K)
       LA = NZ(L)
C
```

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```
C      ALLOW H2(55), CO2(40) AND H2O(49) AS PRODUCTS ONLY
       IF( IA .EQ. 55 .OR. IA .EQ. 40 .OR. IA .EQ. 49) GOTO 20
       IF( JA .EQ. 55 .OR. JA .EQ. 40 .OR. JA .EQ. 49) GOTO 20
C
C      FIND NZ(SPECIES M) -- SPECIES NUMBER OF THE SPECIAL SPECIES M
C
       DO 201 IFM = 1, N
       IF(C(IFM) .NE. 0 .OR. O(IFM) .NE. 0 .OR. H(IFM) .NE. 0) GOTO 201
       NM = NZ(IFM)
       GOTO 202
  201  CONTINUE
  202  CONTINUE
C      ALLOW ISOMERIZATIONS ONLY WITH M
       IF((IA.NE.NM.AND.JA.NE.NM).AND.(IA.EQ.KA .OR. IA.EQ.LA .OR.
     &     JA.EQ.KA .OR. JA.EQ.LA)) GOTO 20
C      ONLY ALLOW THF(38),1-BUTENE(36) AND T-BUTENE(35) AS PRODUCTS
C          OF ISOMERIZATIONS
       IF((KA.EQ.38 .OR. KA.EQ.36 .OR. KA.EQ.35 .OR. LA.EQ.38 .OR.
     & LA.EQ.36 .OR. LA.EQ.35) .AND. (IA.NE.NM .AND. JA.NE.NM)) GOTO20
C
       DELH=(ENTL(K)+ENTL(L))-(ENTL(I)+ENTL(J))
       DELS = (ENTR(K)+ENTR(L)) - (ENTR(I)+ENTR(J))
       DELG = DELH - TEMP * DELS
       IF(DELG .GT. 20.0 .OR. DELH .GT. 35.0) GOTO 20
C
C      MAKE CHECKS BY THE NUMBER OF BONDS FORMED AND BROKEN
C
       NCHD = NCH(KA) + NCH(LA) - NCH(IA) - NCH(JA)
       NCCD = NCC(KA) + NCC(LA) - NCC(IA) - NCC(JA)
       NCOD = NCO(KA) + NCO(LA) - NCO(IA) - NCO(JA)
       NOOD = NOO(KA) + NOO(LA) - NOO(IA) - NOO(JA)
       NOHD = NOH(KA) + NOH(LA) - NOH(IA) - NOH(JA)
       NET = IABS(NCCD)+IABS(NCHD)+IABS(NOOD)+IABS(NOHD)+IABS(NCOD)
C
C      SET SOME CRITERIA FOR MAXIMUM NUMBER OF BOND CHANGES ALLOWED
C       IN A SPECIFIC REACTION.
C
       IF(NET .GT. 3) GOTO 20
C
C      ALLOWS 3 BOND CHANGES IF CO2(40) IS FORMED OR IF 2 RADICALS
C         FORM 2 STABLE SPECIES.
       IF((NET.EQ.3).AND.(KA.EQ.40.OR.LA.EQ.40)) GOTO 90
       IF((NET.EQ.3).AND.(IA.GT.27.OR.JA.GT.27.OR.KA.LT.28.OR.LA.LT.28))
     &   GOTO 20
   90 CONTINUE
C
       IF(IABS(NCOD) .GT. 2) GOTO 20
       IF(IABS(NCCD) .GT. 1) GOTO 20
       IF(IABS(NCHD) .GT. 2) GOTO 20
       IF(IABS(NOOD) .GT. 2) GOTO 20
       IF(IABS(NOHD) .GT. 1) GOTO 20
C      ADD SPECIFIC CHECKS
C      ALLOW CO(44) TO GO TO ONLY CO2(40) OR M(4)
       IF((IA.EQ.44.OR.JA.EQ.44).AND.(KA.NE.40.AND.KA.NE.4.AND.LA.NE.4
     &    .AND.LA.NE.40)) GOTO 20
```

```
PAGE 0004  RXNGN  9:38 AM  THU., 16  JULY, 1981

C       ALLOW CH4(50) TO GO TO ONLY CH3(26)
        IF((IA.EQ.50 OR.JA.EQ.50).AND. (KA.NE.26 AND.LA.NE.26)) GOTO 20
C       ALLOW C2H6(30) TO GO TO ONLY C2H5(7)
        IF((IA.EQ.30.OR.JA.EQ.30).AND. (KA.NE.7 .AND.LA.NE.7 )) GOTO 20
C       ALLOW C3H8(54) TO GO TO ONLY CH3CH2CH2(11) OR CH3CHCH3(12)
        IF((IA.EQ.54 OR.JA.EQ.54) AND. (KA.NE.11 AND.KA.NE.12 .AND.
       &   LA.NE.11.AND.LA.NE.12)) GOTO 20
C       ALLOW C4H10(37) TO GO TO ONLY CH3CH2CHCH3(15) OR CH3CH2CH2CH2(14)
        IF((IA.EQ.37.OR.JA.EQ.37).AND. (KA.NE.14.AND.KA.NE.15 .AND.
       &   LA.NE.14.AND.LA.NE.15)) GOTO 20
C       ALLOW CH3O(5) TO GO TO SOMETHING WITH ZERO OR ONE CARBON
        IF((IA.EQ.5.OR.JA.EQ.5).AND. (C(K).NE.0.AND.C(K).NE.1.AND.
       &   C(L).NE.0 .AND. C(L).NE.1)) GOTO 20
C       ALLOW H(1) TO GO TO ONLY M(4), H2(55), H2O(49), OR H2O2(41)
        IF((IA.EQ.1.OR.JA.EQ.1).AND.(KA.NE.4.AND.KA.NE.55.AND.KA.NE.49
       &     AND. KA.NE.41 AND.LA.NE.4 AND.LA.NE.55 AND.LA.NE.49
       &    .AND. LA.NE.41))GOTO 20
C       ALLOW OH(2) TO GO TO ONLY M(4), H2O(49), HO2(3), AND H2O2(41)
        IF((IA.EQ.2 OR.JA.EQ.2).AND.(KA.NE.4 AND.KA.NE.49 AND.KA.NE.3.AND.
       &   KA.NE.41.AND.LA.NE.4 AND.LA.NE.49 AND.LA.NE.3.AND.LA.NE.41))
       &   GOTO 20
C       DON'T ALLOW CERTAIN GROUPS OF ISOMERS TO INTERCONNECT UNLESS M(4)
C       IS INVOLVED.  GROUP I (11, 52, 25, 22) WILL NOT CONNECT WITH
C       GROUP II (12, 53, 13, 23).  GROUP III (14, 16, 20, 47) WILL
C       NOT CONNECT WITH GROUP IV (15, 18, 27, 46).
        IF((IA.EQ.11.OR.IA.EQ.52.OR.IA.EQ.25.OR.IA.EQ.22.OR.JA.EQ.11.OR.
       &     JA.EQ.52.OR.JA.EQ.25 OR.JA.EQ.22) .AND. (KA.EQ.12.OR.KA.EQ.53
       &      OR.KA.EQ.13.OR.KA.EQ.23.OR.LA.EQ.12.OR.LA.EQ.53 OR.LA.EQ.13
       &      OR.LA.EQ.23) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
        IF((IA.EQ.12.OR.IA.EQ.53.OR.IA.EQ.13.OR.IA.EQ.23.OR.JA.EQ.12.OR.
       &     JA.EQ.53.OR.JA.EQ.13 OR.JA.EQ.23) .AND. (KA.EQ.11.OR.KA.EQ.52
       &      OR.KA.EQ.25.OR.KA.EQ.22.OR.LA.EQ.11.OR.LA.EQ.52.OR.LA.EQ.25
       &      OR.LA.EQ.22) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
        IF((IA.EQ.14.OR.IA.EQ.16.OR.IA.EQ.20 OR.IA.EQ.47 OR.JA.EQ.14.OR.
       &     JA.EQ.16.OR.JA.EQ.20.OR.JA.EQ.47).AND.(KA.EQ.15.OR.KA.EQ.18
       &      OR.KA.EQ.27 OR.KA.EQ.46.OR.LA.EQ.15.OR.LA.EQ.18 OR.
       &    LA.EQ.27.OR.LA.EQ.46)  AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
        IF((IA.EQ.15.OR.IA.EQ.18.OR.IA.EQ.27 OR.IA.EQ.46 OR.JA.EQ.15.OR.
       &     JA.EQ.18.OR.JA.EQ.27 OR.JA.EQ.46) .AND. (KA.EQ.14 OR.KA.EQ.16
       &     .OR.KA.EQ.20.OR.KA.EQ.47.OR.LA.EQ.14 OR.LA.EQ.16.OR.LA.EQ.20
       &      OR.LA.EQ.47) .AND. (IA.NE.NM .OR. JA.NE.NM)) GOTO 20
C       ALLOW METHANE (50) TO COME FROM METHYL (26) ONLY
        IF((KA.EQ.50.OR.LA.EQ.50)  AND. (IA.NE.26.AND.JA.NE.26)) GOTO 20
        JJ = JJ + 1
        WRITE(LP,107)(NAME(IZ,I),IZ=1,4),IA,(NAME(IZ,J),IZ=1,4),JA,
       &(NAME(IZ,K),IZ=1,4),KA,(NAME(IZ,L),IZ=1,4),LA,
       &DELH,DELG,II,JJ,NCHD,NCCD,NCOD,NOOD,NOHD,NET
     20 CONTINUE
     30 CONTINUE
     40 CONTINUE
     50 CONTINUE
C
C       WRITE OUT TOTAL COMBINATIONS TRIED
C
        WRITE(LP,110) II
```

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PAGE 0005  RKNGN  9:38 AM  THU., 16  JULY, 1981

0221  C      IF WRITING TO TAPE WRITE EOF
0222         IF(LP.EQ.8 .OR. LP .EQ.18) CALL EXEC(3,ICNTL)
0223  C      INDICATE END
0224         WRITE(IP(1),114) II,JJ
0225         END

 FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)

 **  NO WARNINGS **  NO ERRORS **   PROGRAM = 04084      COMMON = 00000
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Appendix B

PROGRAM SELET

```
PAGE 0001  FTN.   9:46 AM  FRI., 17  JULY, 1981

FTN4.L
            PROGRAM SELET(3,99), REV. 800710 DOREN INDRITZ
C           VERSION 800710 FOR HEWLETT PACKARD MINICOMPUTER
C           PROGRAM TO READ A SELECTED DATA FILE FOR SPECIFIED
C                     REACTANT &/OR PRODUCT (ONE SPECIES ONLY)
C            THIS ALLOWS THE CHEMIST TO FOLLOW THE REACTIONS OF
C             A PARTICULAR SPECIES IN A LARGE MECHANISM.
C
C           LOGICAL LOG TELLS TRUTH OF MATCHES
            LOGICAL LOG
            DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),
           &          ISLCT(8),IMAS(8)
C           ICR IS THE CARTRIDGE THAT THE DATA FILE IS ON.
C           NMAT IS THE NUMBER OF SUCCESSFUL MATCHES.
C           IPL IS ASCII "+", USED TO LOCATE POSITION IN FILE.
C           ISLCT ARE THE COLUMNS IN THE DATA FILE CORRESPONDING TO
C            THE SPECIES NUMBERS
            DATA ICR,ISC,NMAT,IPL,IL/27,0,0,25400B,132/
            DATA ISLCT/12,13,27,28,43,44,58,59/
C
C           FORMATS
C
        100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
        101 FORMAT(3A2)
        102 FORMAT(' IER = ',I8)
        103 FORMAT(' WHICH SPECIES NUMBER ARE YOU INTERESTED IN?')
        104 FORMAT(132A1)
        105 FORMAT(' ',132A1)
        106 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,
          &        ' AS A PRODUCT'///)
        107 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,
          &        ' AS A REACTANT'///)
        108 FORMAT('1REACTIONS INVOLVING SPECIES NUMBER',I3,' AS A REACTANT',
          !        ' OR A PRODUCT'///)
        109 FORMAT(' DO YOU WISH TO EXAMINE SPECIES NUMBER',I3,' AS ',
            &      /' A REACTANT ONLY? = 1'/' A PRODUCT ONLY? = 2'/
            &      ' OR AS A PRODUCT AND A REACTANT? = 3')
        110 FORMAT(//' SELECTION PROCESS FINISHED. A TOTAL OF ',I3,
          &        ' SELECTED.')
        111 FORMAT(10X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
            &      4X,'#TRD',2X,'#FND',3X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
            &      'NOOD',1X,'NOHD',2X,'NET'//)
C
C
C           GET LOGICAL UNIT NUMBER(LU) OF DIALOGUE DEVICE
            CALL RMPAR(IP)
C           SET LU FOR LIST DEVICE
            LP = 06
C           GET NAME OF DATA FILE
            WRITE(IP(1),100)
            READ(IP(1),101) (NAMF(K),K = 1, 3)
C           GET THE NUMBER OF THE SPECIES TO DO THE SEARCH ON
            WRITE(IP(1),103)
C           NOTE "*" FORMAT IS FREE FORM INPUT.
            READ(IP(1),*) IMATCH
```

PAGE 0002 SELET 9:46 AM FRI., 17 JULY, 1981

```
C      ASK IF USER WISHES SEARCH AS REACTANT ONLY, PRODUCT ONLY OR
C       OR AS REACTANTS AND PRODUCTS
     1 WRITE(IP(1),109) IMATCH
       READ(IP(1),*) IBR
C      MAKE SURE USER GAVE A LEGITIMATE RESPONSE
       IF(IBR.LT.1 .OR. IBR .GT. 3) GOTO 1
C      ASSIGN CORRECT FORMAT FOR OUTPUT DEPENDING ON RESPONSE
       IF(IBR .EQ. 1) ASSIGN 107 TO ITIT
       IF(IBR .EQ. 2) ASSIGN 106 TO ITIT
       IF(IBR .EQ. 3) ASSIGN 108 TO ITIT
       WRITE(LP,ITIT) IMATCH
       WRITE(LP,111)
C
C      OPEN DATA FILE ON DISK #ICR
       CALL OPEN(IDCB,IER,NAMF,0,ISC,ICR)
C      CHECK FOR ERROR RETURN
       IF(IER .LT. 0) WRITE(IP(1),102) IER
C
C      READ IN A LINE OF DATA
     7 CALL READF(IDCB,IER,IBUFR,IL,LEN)
C      CHECK FOR ERROR RETURN
       IF(IER .LT. 0) WRITE(IP(1),102) IER
C      CHECK FOR END OF FILE (EOF)
       IF(IER .EQ. -12) GOTO 25
C
C      CALL CODE READ DOES A FORMATTED READ OF THE FILE.
       CALL CODE
       READ(IBUFR,104) (IBUF(I), I = 1, 132)
C
C      LOOK FOR FIRST REACTION (LOOK FOR A PLUS SIGN)
C
       IF(IAND(IBUF(16),IPL) .NE. IPL) GOTO 7
C
C      CONVERT SELECTED PORTIONS FROM ASCII TO NUMBERS INTERNAL TO THE
C       COMPUTER   ISLCT POINTS TO CORRECT COLUMNS OF DATA FILE.
C
       DO 10 I = 1, 8
       IMAS(I) = IBUF(ISLCT(I))
       IMAS(I) = IAND(IMAS(I),37400B)/400B
       IF(IMAS(I) .EQ. 40B) IMAS(I) = IMAS(I) + 20B
       IMAS(I) = IMAS(I) - 60B
    10 CONTINUE
C      RECONSTRUCT NUMBERS IA & JA FOR REACTANTS, KA & LA FOR PRODUCTS.
       IA = 10 * IMAS(1) + IMAS(2)
       JA = 10 * IMAS(3) + IMAS(4)
       KA = 10 * IMAS(5) + IMAS(6)
       LA = 10 * IMAS(7) + IMAS(8)
C
C       LOOK FOR MATCHES
C
       GOTO(11,12,13), IBR
C
C      REACTANT ONLY
C
    11 LOG = IMATCH .EQ. IA  .OR. IMATCH .EQ. JA
```

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PAGE 0003  SELET  9:46 AM  FRI., 17  JULY, 1981

             GOTO 20
      C
      C      PRODUCTS ONLY
      C
          12 LOG = IMATCH .EQ. KA .OR. IMATCH .EQ. LA
             GOTO 20
      C
      C      REACTANT &/OR PRODUCT
      C
          13 LOG = IMATCH .EQ. IA .OR. IMATCH .EQ. JA .OR. IMATCH .EQ. KA
            &        .OR. IMATCH .EQ. LA
      C
      C      OUTPUT TO LIST DEVICE
      C
          20 IF(LOG) WRITE(LP,105) (IBUF(I), I = 1, 126)
             IF(LOG) NMAT = NMAT + 1
      C
      C      CHECK FOR EOF
      C
             IF(IER .NE. -12) GOTO 7
        25   CONTINUE
      C
      C      EOF
      C
      C      WRITE NUMBER OF MATCHES TO LIST DEVICE AND TO DIALOGUE DEVICE.
             WRITE(LP,110) NMAT
             WRITE(IP(1),110) NMAT
             END


 FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)

 **  NO WARNINGS **  NO ERRORS **   PROGRAM = 01228      COMMON = 00000
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Appendix C
PROGRAM SLRXT

```
PAGE 0001  FTN.    9:57 AM  FRI., 17  JULY, 1981

FTN4,L
      PROGRAM SLRXT(3,99), REV. 800813 DOREN INDRITZ
C     VERSION 800813 FOR HP MINICOMPUTER
C
C     PROGRAM TO READ A SELECTED DATA FILE FOR SPECIFIED
C             REACTANTS &/OR PRODUCTS
C     THIS PROGRAM ALLOWS ONE TO SELECT MULTIPLE INPUTS (<=20) AS
C      REACTANTS.  THUS ALLOWING ONE TO SELECT CLASSES OF
C      REACTIONS.  (DIFFERS FROM &SELET, WHICH ALLOWS ONLY ONE.)
C
C     LOG IS LOGICAL FOR REACTANT SPECIES MATCH
C     LOG2 IS LOGICAL FOR COMPLEMENTARY REACTIONS
      LOGICAL LOG,LOG2
      DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),
     &          ISLCT(8),INAS(8),IIN(20),JIN(20)
      DATA ICR,ISC,NMAT,IPL,IL/27,0,0,254008,132/,IYES/2HYE/
      DATA ISLCT/12,13,27,28,43,44,58,59/
C
C     FORMATS
C
  100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
  101 FORMAT(3A2)
  102 FORMAT(' IER = ',I8)
  103 FORMAT(' HOW MANY "IA" REACTANTS ARE YOU INTERESTED IN?')
  104 FORMAT(132A1)
  105 FORMAT(' ',132A1)
  106 FORMAT(' ENTER SPECIES -> ')
  107 FORMAT('1REACTIONS INVOLVING SPECIES AS REACTANTS-> ', ,1X,20I3)
  108 FORMAT(' DO YOU WANT TO SPECIFY COMPLEMENTARY REACTANTS?')
  109 FORMAT(A2)
  110 FORMAT(//' SELECTION PROCESS FINISHED. A TOTAL OF ',I3,
     &       ' SELECTED.')
  111 FORMAT(10X,'REACTANTS',22X,'PRODUCTS',18X,'DELH',8X,'DELG',
     &       4X,'#TRD',2X,'#FND',3X,'NCHD',1X,'NCCD',1X,'NCOD',1X,
     &       'NOOD',1X,'NOHD',2X,'NET'//)
  112 FORMAT(' THIS PROGRAM ALLOWS YOU TO SELECT UP TO 20 REACTANTS')
  113 FORMAT(' HOW MANY "JA" REACTANTS ARE YOU INTERESTED IN?')
  114 FORMAT(' COMPLEMENTARY REACTANTS -> ',20I3)
C
C
C     OBTAIN LOGICAL UNIT NUMBER(LU) OF INPUT DEVICE FOR DIALOGUE.
      CALL RMPAR(IP)
C     LP IS LU FOR OUTPUT LISTING
      LP =  06
      WRITE(IP(1),112)
C     OBTAIN NAME OF DATA FILE
      WRITE(IP(1),100)
      READ(IP(1),101) (NAMF(K),K = 1, 3)
C     OBTAIN NUMBER OF REACTANTS
      WRITE(IP(1),103)
      READ(IP(1),*) NII
C     OBTAIN NUMBERS OF THOSE REACTANTS
C     HAVE TO REFER TO ORIGINAL DATA INPUT FILE TO SEE SPECIES NUMBERING
      WRITE(IP(1),106)
      READ(IP(1),*) (IIN(LL), LL = 1, NII)
```

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PAGE 0002  SLRXT  9:57 AM  FRI., 17  JULY, 1981

C      SEE IF USER WANTS TO SPECIFY COMPLEMENTARY REACTANTS
       WRITE(IP(1),108)
       READ(IP(1),109) IANS
       IF(IANS .EQ. IYES) LOG2 = .TRUE.
       IF( .NOT. LOG2) GOTO 9
C      OBTAIN NUMBER OF COMPLEMENTARY REACTANTS
       WRITE(IP(1),113)
       READ(IP(1),*) NJJ
C      OBTAIN THE NUMBERS OF THOSE REACTANTS
       WRITE(IP(1),106)
       READ(IP(1),*) (JIN(LL), LL = 1, NJJ)
    9  CONTINUE
C      WRITE HEADER WHICH INCLUDES REACTANT SPECIES NUMBERS
       WRITE(LP,107) (IIN(L),L=1,NII)
       IF(LOG2) WRITE(LP,114) (JIN(L), L = 1, NJJ)
       WRITE(LP,111)
C
C      OPEN DATA FILE FROM DISK
       CALL OPEN(IDCB,IER,NAMF,0,ISC,ICR)
C      CHECK FOR ERROR RETURN
       IF(IER .LT. 0) WRITE(IP(1),102) IER
C
C      READ IN DATA LINE AT A TIME
     7 CALL READF(IDCB,IER,IBUFR,IL,LEN)
C      CHECK FOR ERROR RETURN
       IF(IER .LT. 0) WRITE(IP(1),102) IER
C      CHECK FOR END OF FILE (EOF)
       IF(IER .EQ. -12) GOTO 25
C
C      READ FILE WITH FORMAT.  NOTE THAT A READF CALL GETS RECORD
C      FROM FILE AS IS.  CALL CODE READ DOES A FORMATTED READ OF THE
C      FILE.  HP IS SUPPOSED TO COME OUT WITH A SOFTWARE REVISION
C      THAT ALLOWS FOR DIRECT READING OF A NAMED FILE.
       CALL CODE
       READ(IBUFR,104) (IBUF(I), I = 1, 132)
C
C      LOOK FOR FIRST REACTION (LOOK FOR A PLUS SIGN)
C
       IF(IAND(IBUF(16),IPL) .NE. IPL) GOTO 7
C
C      CONVERT SELECTED PORTIONS FROM KNOWN FORMAT INTO NUMBERS
C      INTERNAL TO THE COMPUTER.
C
       DO 10 I = 1, 8
C      FOLLWING LINE TOGETHER WITH DATA STATEMENT FOR ISLCT GETS
C      CHARACTERS FROM SPECIFIC COLUMNS OF DATA FILE
       IMAS(I) = IBUF(ISLCT(I))
       IMAS(I) = IAND(IMAS(I),37400B)/400B
       IF(IMAS(I) .EQ. 40B) IMAS(I) = IMAS(I) + 20B
       IMAS(I) = IMAS(I) - 60B
   10  CONTINUE
       IA = 10 * IMAS(1) + IMAS(2)
       JA = 10 * IMAS(3) + IMAS(4)
C      KA AND LA ARE THE NUMBERS OF THE PRODUCTS FOR EACH REACTION.
C      THEY ARE NOT USED IN THIS PROGRAM.  THE INFORMATION IS INCLUDED
```

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PAGE 0003  SLRXT  9:57 AM  FRI., 17  JULY, 1981

C      HERE SO THAT ONE CAN EASILY SEE HOW TO IMPLEMENT A SEARCH FOR
C      SPECIFIC PRODUCTS.
C      KA = 10 * IMAS(5) + IMAS(6)
C      LA = 10 * IMAS(7) + IMAS(8)
C
C
C      IF WE ARE LOOKING FOR REACTIONS OF SPECIES WITH SPECIFIED
C       COMPLEMENTARY REACTANTS, JUMP AHEAD TO LINE 21.
       IF(LOG2) GOTO 21
       DO 15 II = 1, NII
       LOG = .FALSE.
C      SEE IF SPECIFIED REACTANTS OCCUR IN POSITION IA OR JA.
       IF(IIN(II) .NE. IA .AND. IIN(II) .NE. JA ) GOTO 15
       LOG = .TRUE.
       GOTO 20
   15  CONTINUE
       GOTO 22
C
C      LOOK FOR MATCHES OF BOTH SPECIES AND COMPLEMENTARY REACTANTS
   21  CONTINUE
       DO 30 II = 1, NII
       DO 30 JJ = 1, NJJ
       LOG = .FALSE.
       IF((IIN(II) .EQ. IA .AND. JIN(JJ) .EQ. JA) .OR. (IIN(II) .EQ. JA
      &   .AND. JIN(JJ) .EQ. IA)) LOG = .TRUE.
       IF(LOG) GOTO 20
    30 CONTINUE
C
C      OUTPUT REACTION MATCHED
C
    20 IF(LOG) WRITE(LP,105) (IBUF(I), I = 1, 126)
C      COUNT NUMBER OF MATCHES
       IF(LOG) NMAT = NMAT + 1
C
C      CHECK FOR EOF, IF NOT EOF, CONTINUE READING
C
    22 CONTINUE
       IF(IER .NE. -12) GOTO 7
  25   CONTINUE
C
C      EOF
C
C      IF EOF WRITE NUMBER OF MATCHES TO LISTING DEVICE AND TO DIALOGUE
C      DEVICE.
       WRITE(LP,110) NMAT
       WRITE(IP(1),110) NMAT
       END


 FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)


 **  NO WARNINGS **  NO ERRORS **   PROGRAM = 01357      COMMON = 00000
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Appendix D
PROGRAM RLIST

```
PAGE 0001  FTN.   9:12 AM  WED., 22  JULY, 1981

FTN4,L
      PROGRAM RLIST(3,99), REV. 810420 DOREN INDRITZ
C     VERSION 810420 FOR HEWLETT PACKARD MINICOMPUTER
C     TO LIST REACTION FILE, DOUBLE SPACED.
C      IN SHORTENED FORMAT (ONLY FIRST 60 COLUMNS PLUS THE
C      NUMBER LISTED UNDER "#FND")   THIS GIVES A LISTING
C      THAT HAS ROOM TO MAKE COMMENTS IN THE RIGHT HAND "MARGIN",
C      BUT STILL KEEPS REQUISITE IDENTIFIERS.
C      ECHOS DATA AT HEAD OF FILE UNTIL FINDS FIRST REACTION.
C      PROGRAM COUNTS NUMBER OF REACTIONS FOUND IN THE FILE.
C
      DIMENSION IP(5),NAMF(3),IBUFR(132),IBUF(132),IDCB(144),INAS(5)
      DATA ICR,ISC,NMAT,IPL,IL,IBLBL/27,0,0,25400B,132,2H  /
C     ICR IS THE CARTRIDGE THAT THE DATA FILE IS ON
C     IPL IS ASCII FOR "+" IN THE LEFT BYTE.
C
C     FORMATS
C
  100 FORMAT(' ENTER DATA FILE NAME (6 CHARACTERS)')
  101 FORMAT(3A2)
  102 FORMAT(' IER = ',I8)
  103 FORMAT(132A1)
  104 FORMAT(1H0,60A1,1X,I4)
  105 FORMAT(' FINISHED   A TOTAL OF ',I3,' WRITTEN.')
C
C     OBTAIN LOGICAL UNIT NUMBER(LU) OF DIALOGUE DEVICE.
      CALL RMPAR(IP)
C     SET LU FOR LIST DEVICE
      LP = 9
C     OBTAIN NAME OF DATA FILE
      WRITE(IP(1),100)
      READ(IP(1),101) (NAMF(K), K = 1, 3)
C
C     OPEN DATA FILE FOR READING.
      CALL OPEN(IDCB,IER,NAMF,0,ISC,ICR)
      IF(IER .LT. 0) WRITE(IP(1),102) IER
    7 DO 10 I = 1, 132
      IBUFR(I) = IBLBL
   10 CONTINUE
      CALL READF(IDCB,IER,IBUFR,IL,LEN)
      IF(IER .LT. 0) WRITE(IP(1),102) IER
      IF(IER .EQ. -12) GOTO 25
C
C      CALL CODE READ DOES A FORMATTED READ OF A SPECIFIED BUFFER.
      CALL CODE
      READ(IBUFR,103) (IBUF(I), I = 1, 132)
C
C     LOOK FOR FIRST REACTION (" + " SIGN)
C
      IF(IAND(IBUF(16),IPL) .EQ. IPL) GOTO 8
      WRITE(LP,103) (IBUF(L),L=1,132)
      GOTO 7
C
C     GET #FND, THIS WILL BE PART OF THE OUTPUT
C
```

```
PAGE 0002  RLIST  9:12 AM  WED., 22  JULY, 1981

      8  DO 20 I = 1, 5
         IMAS(I) = IAND(IBUF(85+I),37400B)/400B
         IF(IMAS(I) .EQ. 40B) IMAS(I) = IMAS(I) + 20B
         IMAS(I) = IMAS(I) - 60B
     20  CONTINUE
         NFND = 10000*IMAS(1)+1000*IMAS(2)+100*IMAS(3)+10*IMAS(4)+IMAS(5)
C
         WRITE(LP,104) (IBUF(I),I = 1, 60), NFND
C        KEEP TRACK OF THE NUMBER OF MATCHES.
         NMAT = NMAT + 1
C
C        CHECK FOR EOF
         IF(IER .NE. -12) GOTO 7
     25  CONTINUE
C
         WRITE(LP,105) NMAT
         WRITE(IP(1),105) NMAT
         END


FTN4 COMPILER: HP92060-16092 REV. 2026 (800423)


**  NO WARNINGS **  NO ERRORS **   PROGRAM = 00815      COMMON = 00000
```

END

DATE
FILMED

11-81

DTIC